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FORCE CONSTANTS FOR UNLIKE MOLECULAR INTERACTIONS ON EXP-SIX MODEL FROM INTER-DIFFUSION

R. PAUL

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

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ABSTRACT. Force constants for unlike molecular interactions for the systems Ne–A, Ne–Kr, A–Kr, He–A, A–Xe, He–Xe, He–Kr and Ne–Xe have been determined on the exponential six model from temperature dependence of inter-diffusion coefficients. To simplify matters, the values of α_{12} were taken to be those obtained from the temperature dependence of thermal diffusion or from the combination rules and the method of intersection was employed to give r_{12} and $(r_m)_{12}$. The force constants, thus obtained, have been compared with the values obtained from other methods and satisfactory agreement has been obtained. These force constants have been used to calculate the thermal diffusion factors at different temperatures and reasonable agreement has been obtained except in the case of A Kr

INTRODUCTION

The inter-molecular potentials for like molecules have been determined accurately for many molecules by a large number of workers. For this purpose, various transport properties of gases, specially viscosity, have been utilised. However, there is considerable uncertainty in the values of unlike force constants for most of the molecular pairs, as there is lack of suitable accurate experimental data over a large temperature range. The transport properties of gas mixtures depend on both like and unlike force parameters, and in cases of viscosity and thermal conductivity the like molecular interaction tends to mask the effect of unlike interactions. In case of thermal diffusion, the masking is reduced, and for inter-diffusion it is insignificant. Unfortunately, until quite recently, sufficiently accurate inter-diffusion data were not available over an extended temperature range. On the other hand, thermal diffusion data being readily available, have been utilised by Srivastava and Madan (1953), Saxena (1955), Srivastava and Srivastava (1957), and Srivastava (1957), for the calculation of the unlike force parameters. Srivastava and Srivastava (1959), and Barua (1959) combined inter-diffusion data with viscosity data to evaluate unlike force constants, which enables even one or two values of the diffusion constant to be utilised.

Recently, several workers (Strehlow, 1953; Bunde 1955; Rumpel, 1955; Srivastava and Srivastava, 1959; Srivastava, 1959; Srivastava and Barua 1959)

have determined D_{12} over a wide range of temperatures and utilised it to determine the unlike force constants on Lennard-Jones 12 . 6 model. In the present paper the values of inter-diffusion coefficients by Srivastava and Srivastava (1959), Srivastava (1959), and Srivastava and Barua (1959) have been used to determine unlike force parameters on the exp-six model. This is of considerable importance as the combination rules so far given are largely emperical and cannot therefore be considered satisfactory.

DETERMINATION OF THE FORCE PARAMETERS

On the Exp-Six model, the potential $\phi(r)$ between two molecules, when separated by a distance r, is given by

$$\phi(r) = \frac{\epsilon}{1-\frac{6}{\alpha}}\left[\frac{6}{\alpha}\, e^{\alpha\left(1-\frac{r}{r_m}\right)} - \left(\frac{r_m}{r}\right)^6\right] \qquad \ldots (1)$$

where ϵ is the depth of the potential energy minimum, r_m is the separation distance for the energy minimum and α is the parameter which gives the steepness of the repulsion energy. The molecular parameters are denoted by $\epsilon_{ij}\,(r_m)_{ij}$ and α_{ij}, where i, j denote the two interacting molecules.

Two sets of combination rules have been recently proposed which enable us to calculate the unlike force parameters in terms of like parameters. The combination rules given by Mason and Rice (1954) are

$$\left[\frac{\epsilon_{12}}{1-\frac{6}{\alpha_{12}}}\,\frac{6}{\alpha_{12}}\,e^{\alpha_{12}}\right] = \left[\left\{\frac{\epsilon_{11}}{1-\frac{6}{\alpha_{11}}}\,\frac{6}{\alpha_{11}}\,e^{\alpha_{11}}\right\}\left\{\frac{\epsilon_{22}}{1-\frac{6}{\alpha_{22}}}\,\frac{6}{\alpha_{22}}\,e^{\alpha_{22}}\right\}\right]^{\frac{1}{2}}$$

$$\frac{\alpha_{12}}{(r_m)_{12}} = \frac{1}{2}\left[\frac{\alpha_{11}}{(r_m)_{11}} + \frac{\alpha_{22}}{(r_m)_{22}}\right] \qquad \ldots (2)$$

$$\frac{\epsilon_{12}(r_m)^6_{12}}{1-\frac{6}{\alpha_{12}}} = \left[\frac{\epsilon_{11}(r_m)^6_{11}}{1-\frac{6}{\alpha_{11}}}\cdot\frac{\epsilon_{22}(r_m)^6_{22}}{1-\frac{6}{\alpha_{22}}}\right]^{\frac{1}{2}}$$

while the following are given by Srivastava and Srivastava (1957)

$$\frac{\alpha_{12}}{(r_m)_{12}} = \frac{1}{2}\left[\frac{\alpha_{11}}{(r_m)_{11}} + \frac{\alpha_{22}}{(r_m)_{22}}\right]$$

$$\epsilon_{12} = (\epsilon_{11}\cdot\epsilon_{22})^{\frac{1}{2}}, \qquad \ldots (3)$$

$$\frac{\epsilon_{12}(r_m)^6_{12}}{1-\frac{6}{\alpha_{12}}} = \left[\frac{\epsilon_{11}(r_m)^6_{11}}{1-\frac{6}{\alpha_{11}}}\cdot\frac{\epsilon_{22}(r_m)^6_{12}}{1-\frac{6}{\alpha_{22}}}\right]^{\frac{1}{2}}$$

These have been used to yield value of α_{12} where this value was not known from the thermal diffusion data.

The procedure adopted for calculating the force constants is as follows :—

The experimental value of D_{12} at different temperatures were plotted and four smoothed out values of D_{12} were taken. Theoretically, D_{12} is given by

$$D_{12} = .002628 \frac{T^{3/2}}{p(r_m)^2_{12}\,\Omega_{12}^{(11)*}(T_{12}^*)} \left[\frac{M_1 + M_2}{2M_1M_2}\right]^{\frac{1}{2}} \quad . \quad (4)$$

where p is the pressure in atmospheres, $T_{12}^* = \frac{kT}{\epsilon_{12}}$, k being the Boltzmann's constant; and $\Omega_{12}^{(11)}$ is a reduced collision integral tabulated by Mason (1954), other symbols having their usual meanings. The values of α_{12} were taken from the previous determinations from thermal diffusion data, where available. In other cases it was calculated from the combination rules given by Srivastava and Srivastava (1957).

From equation (4), substituting a set of values for ϵ_{12}, the corresponding values of $(r_m)_{12}$ were found out using the value of D_{12} at a certain temperature. This was repeated with values of D_{12} at other temperatures, and in this way the values of $(r_m)_{12}$ against ϵ_{12} were plotted and curves were drawn corresponding to each temperature. Since the values of ϵ_{12} and $(r_m)_{12}$ should not vary with temperature, these curves should intersect at a single point. However, due to experimental error, several intersection points occur, fairly close to each other. The mean of all these values gives the required set of force parameters.

In the case where viscosity data on mixture were available, the values of force constants were also determined by combining the viscosity data with inter-diffusion data. The method used for this purpose is essentially the same as that used by Srivastava and Srivastava (1959). Viscosity data were taken from Rietveld, Itterbeek and vanDen Berg (1953) and Trautz and Binkele (1930).

RESULTS

For easy reference the smoothed out values of the inter-diffusion coefficient are recorded in Table I.

In Table II, are tabulated the values of the force constants obtained by the method indicated above, together with the values obtained from a combination of viscosity and mutual diffusion, and from the temperature variation of thermal

diffusion. The respective values from the different combination rules are also given for the sake of comparison

TABLE I

Experimental values of the coefficients of inter-diffusion

Gas pairs	273°K	288°K	303°K	318°K
A-He	0 640	0 701	0 760	0 825
A–Xe	0 0943	0 102	0 114	0.128
He–Xe	0 501	0.550	0 604	0.655
Ne–A	0 276	0.300	0.327	0 357
Ne–Kr	0.223	0 240	0.266	0 284
A–Kr	0 119	0 128	0 140	0 153
He–Kr	0.556	0 605	0.659	0.720
Ne–Xe	0 186	0 202	0.221	0.244

TABLE II

Force Parameters

Gas pair		From intersection	From viscosity and diffusion	From thermal diffusion	Combination rule Srivastava & Srivastava (1957)	Combination rules Mason and Rice (1954)
Ne–A	α_{12}	14.18	14 18	14.18	14 35	14.17
	ε_{12}/k	64 5	66 6	67.6	68.42	73 7
	$(r_m)_{12}$	3 511	3 497	3 504	3 491	3 443
Ne–Kr	α_{12}	13 84		13 81	14 15	13 55
	ε_{12}/k	68 75		73.4	71.74	89 54
	$(r_m)_{12}$	3.725		3 720	3 710	3 549
A–Kr	α_{12}	13.61			13 61	13.52
	ε_{12}/k	128.25			129 2	132 8
	$(r_m)_{12}$	4 123			4 101	4 072
He–A	α_{12}	13.5	13 5	13.5	13 20	13.21
	ε_{12}/k	29 3	31 5	33.4	33.59	33 40
	$(r_m)_{12}$	3 523	3 504	3 471	3 484	3 488
A–Xe	α_{12}	13 4		13 4	13.58	13.44
	ε_{12}/k	173 2.5		170 5	168 8	178 5
	$(r_m)_{12}$	4.200		4 158	4 153	4.108
He–Xe	α_{12}	12 86	12 86		12 86	12 56
	ε_{12}/k	44.2	39.8		46 03	57.88
	$(r_m)_{12}$	3 756	3 803		3.743	3 653
He–Kr	α_{12}	12 89			12.89	12.64
	ε_{12}/k	35.0			35.23	38 73
	$(r_m)_{12}$	3.690			3 696	3 625
Ne–Xe	α_{12}	14 0		14.0	14 15	13.45
	ε_{12}/k	88 88		80.0	93.74	121 8
	$(r_m)_{12}$	3 837		3 799	3 758	3.574

COMPARISON WITH EXPERIMENT

The force constants obtained by the method of intersection are utilised to calculate the thermal diffusion factor at different temperatures. Table III gives the values of α_T, thus obtained together with the experimental values as determined by Grew (1947) and Grew, Johnson and Neal (1954).

TABLE III

Comparison with experimental values of α_T

Gas Pairs	185°K		293°K		465°K	
	Calc	Expt	Calc	Expt	Calc	Expt.
Ne–A	142	148	176	174	194	191(a)
Ne–Kr	220	210	.284	290	319	320(b)
A–Kr	040	032 038	108	060 .075	121	080(a) .149(b)
He–A	368	360	381	380	.	(b)
A–Xe	016	063	100	087	179	176(b)
He–Xe		.	426	434	411	434(b)
He–Kr	397	130	128	448	440	448(b)
Ne–Xe	.205	260	301	300	359	370(b)

Experimental values are of (a) Grew *et al* (1954) and (b) Grew (1947)

REMARKS

It will be seen that the agreement between the calculated and experimental values is very satisfactory except in the case of *A Kr*. This may be due to some errors in the assumed values of the force parameters for Kr in the calculation of α_T. For A-Xe and Ne-Xe the agreement becomes poor at 185°K which seems to be due to Xe approaching its liquefaction point.

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